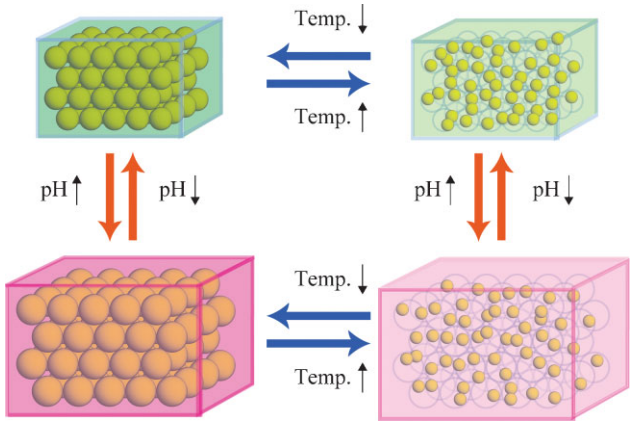
Dual Tuning of the Photonic Band-Gap Structure in Soft Photonic Crystals

By *Masaki Honda, Takahiro Seki,* and *Yukikazu Takeoka**

There is currently an intensive effort to develop photonic crystals that can open up new opportunities in optical and sensing technologies. In photonic crystals, the refractive index varies in a periodic fashion on a length scale that is comparable to the wavelength of light, causing multiple Bragg reflections.[1] This effect prevents light from being transmitted in a range of frequencies known as the photonic band-gap. This property enables the manipulation of electromagnetic waves freely, producing amazing effects that are impossible in conventional optical systems. Most photonic crystals have specific properties that cannot be altered once the crystals are made. These so-called ''passive'' photonic crystals are designed to perform specific functions without any means of external control.

A wide variety of photonic crystals that possess band structures reversibly tunable by external stimuli have been reported in the last decade.[2–6] For future applications in optical devices, such as switching systems, lasers, and displays, it is important to bring the tunability of photonic crystals to fruition. There are various approaches to tuning the photonic band structure. These include infiltrating stimuli-responsive liquid crystals or dyes that can change refractive index into the periodical open structure of the photonic crystal, and mechanically controlling the periodicity of flexible polymer-based photonic crystals. In most cases in which external control of the refractive index has been employed, the changes in the photonic band structure were not notable. In order to increase the tunability of the photonic band structure, particularly of its position (λ_{max}), controlling the periodicity using soft materials such as gels is more powerful. Some groups have reported that soft polymeric materials possessing periodical structures can be used to fabricate tunable photonic crystals. Asher and coworkers developed polymerized crystalline colloidal arrays in which nonclosest-packing colloidal crystals were embedded within stimuli-responsive hydrogels.[3] As the polymerized crystalline colloidal arrays exhibit a change in λ_{max} in the visible range of the electromagnetic spectrum in response to stimuli, Asher and coworkers are developing sensors using these systems. Ozin and coworkers demonstrated tunable photonic crystals composed of unconnected colloidal silica particles in a matrix consisting of a crosslinked redox-active polymer.[4] This colloidal photonic-crystal device exhibits redox and solvent tunability resulting from the anisotropic expansion of the 3D network, and offers potential applications, such as full-color paperlike displays. Our group also created two new tunable soft photonic crystals by templating methods using close-packing silica colloidal crystals (CCCs); one of the crystals involved a wide variety of inverse-opal hydrogels,[5] while the other was made up of confined hydrogel particles in hard inverse-opal polymers.[6] The former systems exhibit a change in λ_{max} in response to external stimuli, while the latter reveal stimuli sensitivity through variation in the intensity of the photonic band-gap, which is measured by the peak intensity of the reflection spectrum. Sensing materials for temperature, pH, redox-active compounds, ionic species, glucose, solvents, light, magnetic fields, and electric fields have been prepared using these systems. However, there have been few reports on independently and extensively tuning both the position and the intensity of the photonic band-gap. The fabrication of photonic crystals with diverse levels of tunability may open doors for their application.

Herein, a dually tunable photonic crystal (DTPC) composed of thermosensitive gel particles confined in a pH-sensitive inverse-opal gel will be proposed (Scheme 1). The proposed structure is very easy to fabricate (see Experimental). The inverse-opal gel consists of a regular arrangement of interconnecting spherical voids surrounded by a pH-sensitive 3D polymer network swollen with aqueous solution. The ordered arrangement of the pore structure leads to the diffraction of light in a manner similar to the diffraction observed in opals. When the pH value of the aqueous solution is altered, a change in the volume of the inverse-opal gel is induced (Fig. 1a),[7] leading to a variation in the periodicity. As a result, λ_{max} can be shifted by the pH of the solution. The degree of swelling of this gel changes very little with temperature. In addition, gel particles confined in the pores of the



Scheme 1. Schematic of DTPCs at different temperatures and in different pH buffer solutions.

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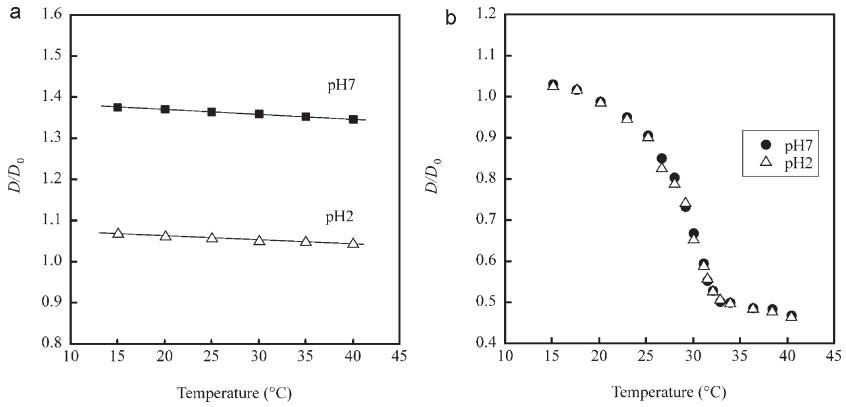

Figure 1. Temperature dependence of the equilibrium swelling degree (D/D_0, where D and D_0 are the thicknesses of the inverse-opal gels in the equilibrium state under a certain condition and in the as-prepared state, respectively) of a) a pH-sensitive inverse-opal gel composed of HEMA, AAc, and EGDMA [7]; and of b) a thermosensitive gel composed of NIPA and BIS in pH 2 and pH 7 buffer solutions. The change in the degree of swelling of the inverse-opal gel in each pH environment is less than 0.03 on increasing the temperature from 15 to 40 °C, whereas a change of about 0.31 is observed at 15 °C on changing the pH from 7 to 2; the size variation of the pH-sensitive inverse-opal gel with temperature is considerably small. The temperature dependence of the NIPA gel was measured using a cylindrical NIPA gel prepared in a glass pipette with an inner diameter of 100 μm. The size change exhibited by the NIPA gel is exactly the same at different pH values: this thermosensitive NIPA gel is not pH-responsive.

inverse-opal gel can change their volumes individually depending on the solution temperature (Fig. 1b). The swelling degree of the thermosensitive gel is pH insensitive. If the pores are completely filled with swollen gel particles, the DTPC is composed of two kinds of gels that form a periodic ordered structure. A clear photonic band-gap can be observed in such a DTPC by measuring the reflection spectrum. However, when the particles collapse, the reflection peak of the DTPC decreases. As observed, the position and intensity of the photonic band-gap in the DTPC could be independently, extensively, and reversibly tuned by temperature and pH.

Figure 2 shows the reflection spectra of a DTPC under different combinations of temperature and pH values. When the pH value is varied between two and seven at a fixed temperature, λ_{max} varies notably, but the peak intensity changes moderately or slightly.

The inverse-opal gel is composed of 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), and ethylene glycol dimethacrylate (EGDMA), while the gel particles are composed of *N*-isopropylacrylamide (NIPA) and *N*,*N*′-methylene-bis-acrylamide (BIS). This HEMA–AAc gel behaves like a neutral polymer network at pH 2, because the pK_a (where K_a is the acid dissociation constant) value of the AAc monomer is 4.25 at 25 °C and, moreover, the pK_a values of AAc copolymerized in polymers are larger than 4.25, as a result of electrostatic interaction between neighboring AAc monomers.[8] All AAc monomers in the HEMA–AAc gel must be in an essentially dissociated state in the pH 7 buffer solution, considering the above-mentioned pK_a values. As a result, the HEMA–AAc gel at pH 7 exhibits dramatic swelling power, resulting from both electrostatic repulsion between the charges on the polymer chains and osmotic pressure of the counterions.[9a] Yet, in salt solutions such as buffer solutions excess cations and anions screen the polymer charges and eliminate the osmotic imbalance; this greatly diminishes the swelling power of the polyelectrolyte gels.[9b] However, in the buffer solutions used in this work, which had an ionic strength of 0.1, the electrostatic repulsion and the osmotic pressure could sufficiently contribute to the increase in the degree of swelling of the HEMA–AAc gel. Thus, the degree of swelling of the HEMA–AAc inverse-opal gel can be tuned in the pH range 2–7 in buffer solutions with an ionic strength lower than 0.1 (Fig. 1a).

We have previously proved that λ_{max} of the inverse-opal gels, observed under normal incidence, can be quantitatively estimated using the equation

$$\lambda_{max} = 1.633\{d\,(D/D_0)/m\}n_a \quad (1)$$

where d is the diameter of the colloidal silica particles used to prepare the template, m is the order of the Bragg diffraction, n_a is the average refractive index calculated considering the indices and the volume fractions of the inverse opal and the spherical particles under certain conditions, and D and D_0 are the thicknesses of the inverse-opal gels in the equilibrium state under a certain condition and in the as-prepared state, respectively.[5h] The change in n_a of the inverse-opal gel is, in most cases, vanishingly small compared with the change in D/D_0 when the volume of the gel changes; the swelling degree is the dominant factor for λ_{max} for the inverse-opal gels.

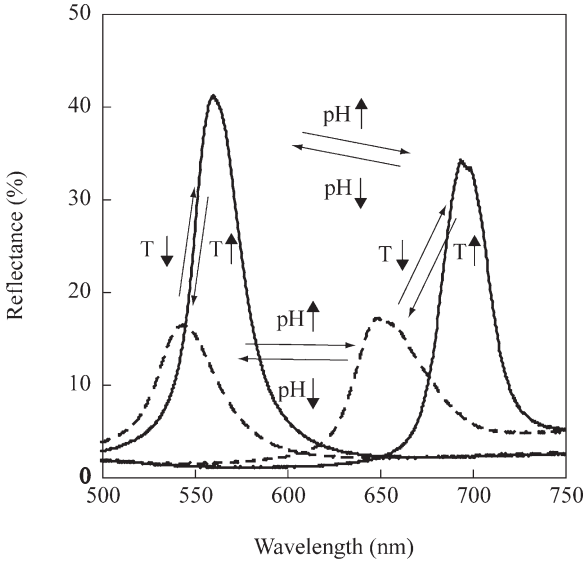

Figure 2. Reflection spectra of a DTPC at different temperatures and in buffer solutions of different pH values. Left solid line: pH 2, 15 °C; right solid line: pH 7, 15 °C; left dashed line: pH 2, 40 °C; right dashed line: pH 7, 40 °C.

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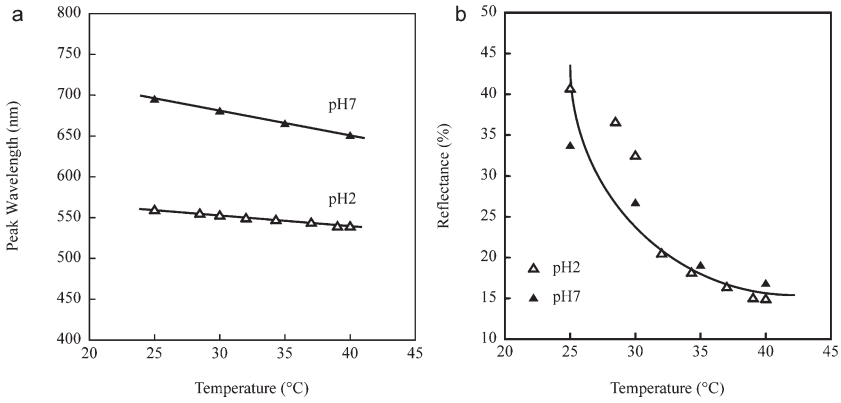


Figure 3. a) λ_{max} of the reflection spectra and b) reflectance of a DTPC as a function of temperature at pH 2 and pH 7.

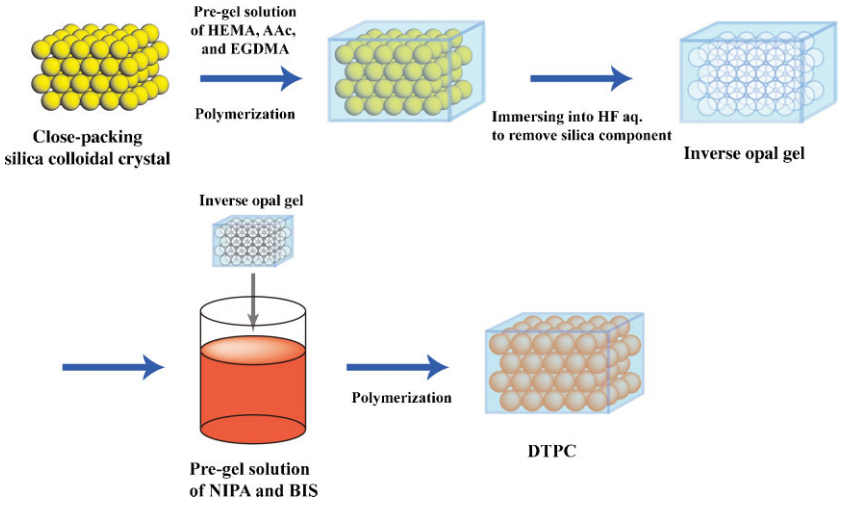
The dependence of λ_{max} on temperature at different pH values is plotted in Figure 3a. In both cases, λ_{max} decreases moderately with increasing temperature. The rise in temperature causes a collapse in the volume of the thermosensitive-gel particles in the DTPC. If all NIPA gel particles are isolated in each pore, the collapsed particles may not have a significant effect on the shape and volume of the inverse-opal gel. Judging by the preparatory procedure of the DTPC, however, an interpenetrating polymer network between the HEMA–AAc polymer network and the NIPA polymer network could be formed, because the inverse-opal gel was slightly swollen in the pregel solution of the NIPA gel. In addition, the isolation procedure of the gel particles (see below) could be imperfect, considering the softness of the inverse-opal gel. These conditions may induce a slight contraction of the inverse-opal gel with increasing temperature. In contrast, as the swelling degree of the inverse-opal gel directly depends on the pH value of the solution, changes in pH have a strong effect on λ_{max}. As above, the position of the photonic band-gap can be predominantly tuned by the solution pH.

Figure 3b shows the temperature dependence of the peak intensity of the reflection spectra of the DTPC at pH 2 and pH 7. The peak intensities change dramatically with temperature, whereas the pH value has little influence on the intensities. This means that the peak intensity can be principally tuned by temperature. Since an increase in temperature causes the collapse of the NIPA-gel particles, the gel particles can move freely and scatter throughout the pores of the inverse-opal gel. This may induce a disturbance in the ordered array of the gel particles, and may form many layers of rough surfaces in the inverse-opal gel. If the gel particles form another periodical structure in the inverse-opal gel with increasing water temperature, a new reflection peak would appear, and its peak intensity would increase as the temperature increases, as a result of amplification of the dielectric contrast.[3a,6b] Our results, however, do not indicate that such was the case, showing instead that the gel-particle array was out of alignment with the contraction of the gel particles. This situation leads to stronger incoherent Mie scattering of light from the gel particles, resulting in a decrease in the coherent Bragg scattering at higher temperatures. It could be that the attenuation of light scattering was caused by thermal motion or quenched disorder: the effect of the Debye–Waller factor.[10]

In summary, dual temperature and pH tuning of the photonic band structure using thermosensitive gel particles confined in a pH-sensitive inverse-opal gel has been described. The position of the photonic band-gap can be thermally regulated, while the intensity of the photonic band-gap is dramatically affected by pH. The reversible, independent, and extensive switching of the position and the intensity of the photonic band-gap could be achieved using different external stimuli. This DTPC has potential for use as a display medium, since not only the hue but also the brightness or saturation of the structural color arising from the photonic band-gap of the DTPC can be controlled by independent external stimuli. Such a full-color display system may also be applicable to sensor systems that can detect multiple stimuli. We believe that this new photonic crystal offers many prospects for simple paperlike displays, high-accuracy sensors, and other optical devices.

Experimental

The dually tunable soft photonic crystal was prepared using a CCC as the starting material (Scheme 2). The CCC was fabricated on a clean glass slide by a solvent-evaporation method, and was used as a template to obtain a pH-sensitive inverse-opal gel. HEMA (Kanto Chemical), AAc (Aldrich), EGDMA (Tokyo Kasei), and 2,2-dimethoxy-2-phenyl acetophenone (Irgacure 651, Acros Organics) were used to prepare the pH-sensitive inverse-opal gel. A solution of HEMA (2.5 g), AAc (69.2 mg), and EGDMA (31.2 mg) containing Irgacure 651 (77.6 mg) was degassed under nitrogen for 20 min and ultrasonically treated for 5 min, and then injected into the CCC in a glass cell consisting of two glass plates separated by a 0.5 mm



Scheme 2. Preparation of a DTPC.

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Teflon spacer. Photopolymerization was performed by light irradiation using a 10 mW Hg–Xe lamp (Supercure-203S, San-ei Electronics) at 25 °C for 5 min, so as to trap the crystalline structure. In this system, no solvent was used to synthesize the gel; the gel obtained was very hard and robust after the reaction. The composite membrane was soaked in 10% hydrofluoric acid solution for several days to remove the silica component completely. The resulting inverse-opal gel membrane with its interconnecting porous structure was washed with water and ethanol to remove unreacted chemicals and the hydrofluoric acid. Subsequently, the weakly crosslinked thermosensitive gel composed of NIPA (Kohjin) as the main monomer and BIS (Kanto Chemical) as crosslinker was prepared by photopolymerization in the pH-sensitive inverse-opal gel. The inverse-opal gel increased slightly in size in the pre-gel solution containing NIPA (824 mM), BIS (82 mM), bis (2,4,6-trimethyl benzoyl) phenylphosphine oxide (Irgacure819, Aldrich, 4.1 mM) as initiator, and ethanol as a solvent. In this work, it was attempted to isolate each gel particle from the covalently interconnecting gel particles by employing a collapse transition of the NIPA gel at high temperature. Each gel particle undergoes a collapse in each compartment above 32 °C, thereby allowing separation of the gel particles. Because of the robust framework of the inverse-opal gel, which is not affected by the mechanical stress caused by high temperatures, each gel particle breaks at the weakest point: the point at which it is connected. After such an operation was repeatedly performed, a DTPC composed of thermosensitive gel particles confined in a pH-sensitive inverse-opal gel was obtained.

The weakly crosslinked cylindrical thermosensitive gels used for observing the swelling characteristics were prepared using the same method used for making the gel particles. The pregel solution was degassed under nitrogen for 20 min, ultrasonically treated for 5 min, and then injected into glass capillary tubes with an internal diameter of 100 μm. Photopolymerization was conducted under the same conditions used for the gel particles. The resulting cylindrical gels were then washed in water to remove unreacted chemicals from the polymer networks.

To measure the pH dependence of the reflection spectra of the DTPC, the pH of the aqueous solution was adjusted by phosphate-buffered salines using phosphoric acid, sodium phosphate, hydrochloric acid, and sodium hydroxide. The ionic strength was adjusted to 0.1 by adding KCl to maintain a constant value in all aqueous solutions. The reflection spectra were obtained using an Ocean Optics USB2000 optical-fiber spectrometer. The equilibrium diameter of the cylindrical gel was measured using a microscope. The temperature in the experiments was controlled by means of a circulating-water temperature-control system.

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[7] The change in the swelling degree of the inverse-opal gel was estimated using the spectroscopically observed values of λ_{max} and Equation 1. The following values were used for each parameter to calculate the value of D/D_0: $d = 233$ nm; $m = 1$. refractive index of water = 1.334; refractive index of the HEMA–AAc gel = 1.435; volume fraction of water spheres = 0.74; and volume fraction of HEMA–AAc gel = 0.26. The n_a value of 1.36 is thus obtained.

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